Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Molecular adsorption at Pt(111). How accurate are DFT functionals ?

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Table S1. Description of the benchmark set for molecular adsorption on Pt(111).
The table lists the integral adsorption energy calculated from the experimental data, at the selected coverage. Mode: M: molecular chemisorption, D: dissociative chemisorption, R: reaction as indicated ((g) is for gas phase, (a) for adsorbed species)
INTF : integration of a fit function provided in ref
INTC : manual integration on the plot of E vs coverage in ref

Molecule / reaction	Exp method	Mode	Coverage for E calc	Energy(eV)	tool	ref
C_2H_4(g) gives CCH_3(a) + H(a)	SCAC	R	1/9 ML	1.36	INTC	1(#)
Cyclohexene	SCAC	M	1/9 ML	1.273	INTF	2
c-C_6H_{10}(g) gives c-C_6H_9(a) + H(a)	SCAC	R	1/9 ML	1.433	INTF	2
Benzene	SCAC	M	1/9 ML	1.72 (1.66)	INTF	3 (4)
Naphthalene	SCAC	M	1/16 ML	2.763	INTF	5
Methane	TPD	M	1/9 ML	0.181	INTF	6
Ethane	TPD	M	1/9ML	0.331	INTF	6
½(H_2 gas)	Low energy recoil scatt	D	1/9 ML(‡)	0.39 ± 0.02	INTC	7
½(H_2 gas)	Nuclear micro-analysis	D	1/9 ML(‡)	0.347 ± 0.04	INTC	8
CO ads	SCAC	M	1/9 ML	1.29 (1.31) 1.29	INTC (INTF) INTC	1(#) 4 9
½ (O_2gas)	SCAC	D	1/9 ML	1.10	INTC	10(#)
½ (O_2gas)	SCAC	D	1/9 ML	1.08	INTF	11

(‡) adsorption energy is constant between 0 and 0.33 ML. (#) Published data incorrect due to wrong reflectivity of Pt(111). Scale factor of 0.7059 applied here.

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Table S2. Adsorption energies (in eV) for various systems and density functional approximations as well as the experimental reference value when available. All calculations were conducted with a slab of 6 layers in a 3x3 supercell except for the adsorption of naphthalene where a 4x4 supercell was used.

Kpts	System	PBE	optPBE	optB86b	BEEF	PBE-dDsC	dDsC[(a)]	Exp
7x7x1	Ethylene	-1.21	-1.44	-1.73	-1.12	-1.51	-0.33	NA
7x7x1	Ethylidyne+H	-1.74	-1.75	-2.15	-1.43	-1.99	-0.28	-1.36
7x7x1	Butene cis	-0.93	-1.52	-1.85	-1.05	-1.51	-0.61	NA
7x7x1	Butene trans	-0.93	-1.53	-1.86	-1.06	-1.51	-0.61	NA
7x7x1	Cyclohexene (boat down)	-0.69	-1.31	-1.62	-0.90			
7x7x1	Cyclohexene (chair trans)	-0.74	-1.37	-1.69	-0.69			
7x7x1	Cyclohexene (chair cis)	-0.75	-1.45	-1.80	-0.95			
7x7x1	Cyclohexene (boat up)	-0.84	-1.51	-1.84	-1.03			
9x9x1	Cyclohexene (boat up)	-0.84	-1.51	-1.83	-1.04	-1.50	-0.66	-1.27
7x7x1	C_6H_9+H	-1.00	-1.63	-2.18	-0.97	-1.73	-0.74	-1.43
9x9x1	C_6H_9+H	-1.01	-1.63	-2.18	-0.98	-1.73	-0.74	-1.43
5x5x1	Butadiene (cis 1,2 di-σ, 3,4 π)	-1.57	-1.99	-2.49	-1.50			
5x5x1	Butadiene (di σ)	-1.00	-1.51	NA	-1.33			
5x5x1	Butadiene(tetra σ)	-1.82	-2.23	-2.78	-1.71			
7x7x1	Butadiene(tetra σ)	--1.89	-2.30	-2.86	-1.75	-2.43	-0.58	NA
9x9x1	Butadiene(tetra σ)	-1.89	-2.30	-2.86	-1.76			NA
7x7x1	Benzene bri30	-1.12	-1.65	-2.34	-1.03	-1.76	-0.71	-1.72
9x9x1	Benzene bri30	-1.12	-1.65	-2.34	-1.04	-1.76	-0.69	-1.72
11x11x1	Benzene bri30	-1.13	-1.66	-2.35	-1.05	-1.76	-0.68	-1.72
11x11x1	Benzene hcp0	-0.86	-1.40	-2.05	-0.82			
7x7x1	Naphtalene[(b)]	-1.48	-2.32	-3.42	-1.41	-2.57	-1.18	-2.76
9x9x1	Naphtalene[(b)]	-1.46	-2.30	-3.39	-1.39	-2.51	-1.14	-2.76
7x7x1	Methane	-0.01	-0.23	-0.21	-0.12	-0.17	-0.10	-0.18
7x7x1	Ethane	-0.03	-0.36	-0.39	-0.22	-0.32	-0.28	-0.33
7x7x1	Hydrogen, fcc site	-0.52	-0.38	-0.50	-0.27	-0.55	-0.05	-0,37
7x7x1	Hydrogen, top site	-0.48	-0.42	-0.50	-0.30	-0.52	-0.06	NA
7x7x1	CO (top)	-1.71	-1.68	-1.87	-1.49	-1.86	-0.16	-1.29
7x7x1	O (fcc)	-1.29	-1.43	-1.50	-1.15	-1.32	-0.07	-1.10

(a) Contribution of the dispersion correction dDsC to the adsorption energy. (b) 4x4 supercell.

Figure S1. Adsorption geometries with characteristic distances indicated. See Table S3 for more details. a: ethylene C_2H_4, b: ethylidyne CCH_3 and one H, c: trans 2-butene C_4H_8, d: cyclohexene C_6H_{10} boat up, e: C_6H_9 and one H, f: butadiene C_4H_6, g: benzene C_6H_6, h: naphthalene $C_{10}H_8$, i: methane CH_4, j: ethane C_2H_6, k: H atom in fcc position, l: CO, m: O atom.

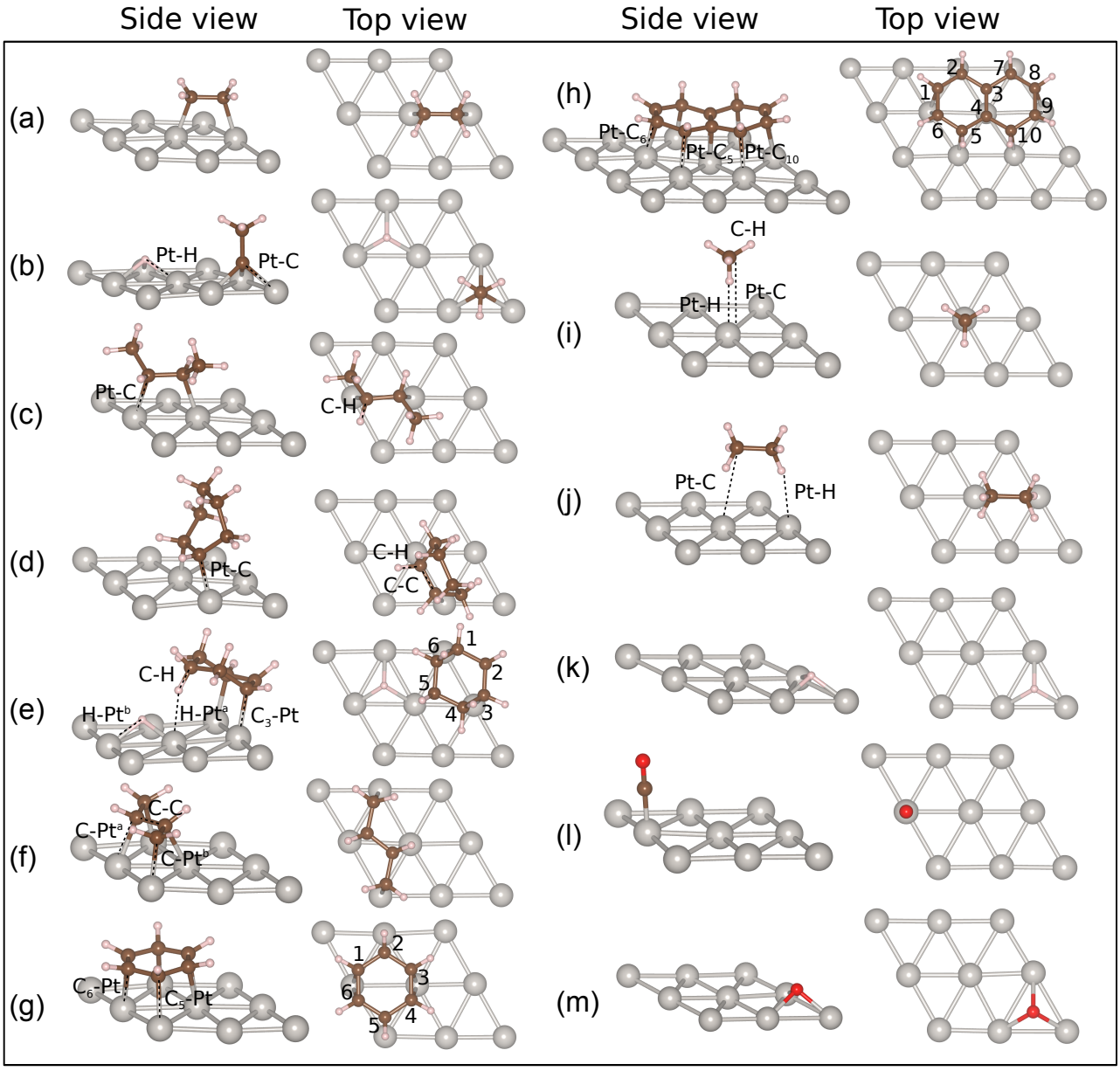

Table S3: Characteristic distances (in Å) for various considered systems.

System	Ethylene		
Distances	Pt-C	C-C	C-H
PBE	2.110	1.489	1.097
optPBE-vdW	2.127	1.491	1.097
optB86b-vdW	2.111	1.49	1.1
BEEF-vdW	2.121	1.487	1.091
PBE-dDsC	2.107	1.487	1.097

System	Ethylidyne+H		
Distances	Pt-C	C-C	Pt-H
PBE	2.013	1.491	1.862
optPBE-vdW	2.022	1.496	1.876
optB86b-vdW	2.013	1.488	1.871
BEEF-vdW	2.012	1.496	1.865
PBE-dDsC	2.011	1.488	1.86

System	Butene trans		
Distances	Pt-C	C-C	C-H
PBE	2.120	1.506	1.102
optPBE-vdW	2.133	1.509	1.101
optB86b-vdW	2.117	1.506	1.105
BEEF-vdW	2.127	1.506	1.095
PBE-dDsC	2.117	1.503	1.101

System	Cyclohexene		
Distances	Pt-C	C-C	C-H
PBE	2.126	1.504	1.102
optPBE-vdW	2.138	1.510	1.102
optB86b-vdW	2.120	1.507	1.106
BEEF-vdW	2.131	1.506	1.096
PBE-dDsC	2.120	1.503	1.101

System	C_6H_9+H										
Distances	C_1C_2	C_2C_3	C_3C_4	C_4C_5	C_5C_6	C_6C_1	H-Pt^a	H-Pt^b	C_2-Pt	C_3-Pt	C-H
PBE	1.496	1.497	1.526	1.522	1.523	1.527	4.089	1.848	2.153	3.081	1.101
optPBE-vdW	1.500	1.500	1.532	1.528	1.529	1.534	4.084	1.854	2.176	3.09	1.102
optB86b-vdW	1.498	1.498	1.526	1.522	1.523	1.527	4.002	1.842	2.152	3.062	1.104
BEEF-vdW	1.496	1.496	1.529	1.525	1.526	1.531	4.135	1.846	2.164	3.09	1.096
PBE-dDsC	1.494	1.494	1.522	1.519	1.519	1.524	4.032	1.847	2.15	3.067	1.1

System	Butadiene		
Distances	C-C	C-Pt-a	C-Pt-b
PBE	1.486	2.159	2.097
optPBE-vdW	1.489	2.181	2.112
optB86b-vdW	1.487	2.16	2.097
BEEF-vdW	1.485	2.174	2.106
PBE-dDsC	1.484	2.156	2.094

System	Benzene								
Distances	C_1C_2	C_2C_3	C_3C_4	C_4C_5	C_5C_6	C_6C_1	Pt-C_5	Pt-C_1	Pt-C_6
PBE	1.474	1.474	1.435	1.473	1.473	1.435	2.158	2.197	2.189
optPBE	1.476	1.475	1.433	1.475	1.475	1.433	2.181	2.23	2.223
optB86b	1.474	1.474	1.435	1.474	1.474	1.435	2.16	2.203	2.194
BEEF	1.472	1.472	1.431	1.472	1.472	1.431	2.173	2.219	2.21
PBE-dDsC	1.472	1.471	1.433	1.471	1.471	1.434	2.156	2.193	2.186

System	Naphtalene										
Distances	C_1C_2	C_2C_3	C_3C_4	C_4C_5	C_5C_6	C_6C_1	C_3C_7	C_7C_8	C_8C_9	C_9C_{10}	$C_{10}C_4$
PBE	1.469	1.485	1.454	1.485	1.469	1.428	1.485	1.469	1.428	1.469	1.484
optPBE	1.471	1.486	1.452	1.487	1.47	1.425	1.486	1.47	1.425	1.471	1.487
optB86b	1.470	1.484	1.452	1.485	1.469	1.427	1.485	1.47	1.427	1.469	1.485
BEEF	1.467	1.483	1.452	1.483	1.466	1.423	1.483	1.467	1.423	1.467	1.483
PBE-dDsC	1.467	1.482	1.452	1.482	1.467	1.427	1.482	1.467	1.427	1.467	1.482

System	Naphtalene			
Distances	Pt-C_1	Pt-C_6	C_5-Pt	C_{10}-Pt
PBE	2.225	2.215	2.221	2.138
optPBE	2.272	2.256	2.261	2.158
optB86b	2.234	2.222	2.229	2.139
BEEF	2.256	2.246	2.242	2.153
PBE-dDsC	2.223	2.213	2.217	2.136

System	Methane		
Distances	Pt-C	C-H	Pt-H
PBE	3.809	1.102	2.713
optPBE-vdW	3.702	1.103	2.606
optB86b-vdW	3.416	1.113	2.307
BEEF-vdW	3.806	1.093	2.719
PBE-dDsC	3.867	1.096	2.766

System	Ethane		
Distances	Pt-C	C-C	Pt-H
PBE	3.86	1.525	2.68
optPBE-vdW	3.628	1.53	2.496
optB86b-vdW	3.465	1.522	2.232
BEEF-vdW	3.865	1.528	2.721
PBE-dDsC	3.874	1.522	2.484

System	Hydrogen	O	CO	
Distances	Pt-H	Pt-O	Pt-C	C-O
PBE	1.868	2.040	1.841	1.157
optPBE-vdW	1.878	2.050	1.853	1.157
optB86b-vdW	1.872	2.038	1.845	1.156
BEEF-vdW	1.869	2.051	1.85	1.156
PBE-dDsC	1.861	2.040	1.84	1.157